

The Ohio State University-School of Earth Sciences

Potential Sources of Salts from Water-Rock Interaction During Hydraulic Fracturing: An Experimental Study

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Introduction

An on-going environmental issue from hydraulic fracturing of gas shale plays is the elevated salt content of flowback fluids¹. Studying this problem is important as the cost and method of disposal of the hydraulic fracturing fluids is dependent on their volume and composition. This study focuses on determining the potential source of salts to flowback fluids from a series of sequential water-rock interaction leach experiments on core samples from the carbonate-rich Point Pleasant Formation and cuttings samples from the clay-rich Utica Formation. The objective is to determine how cation and anion concentrations evolve in solution.

Sample Description and Methods

- Three cuttings samples from the Utica Formation (Table 1).
- Two core samples from the Point Pleasant Formation (Table 1).

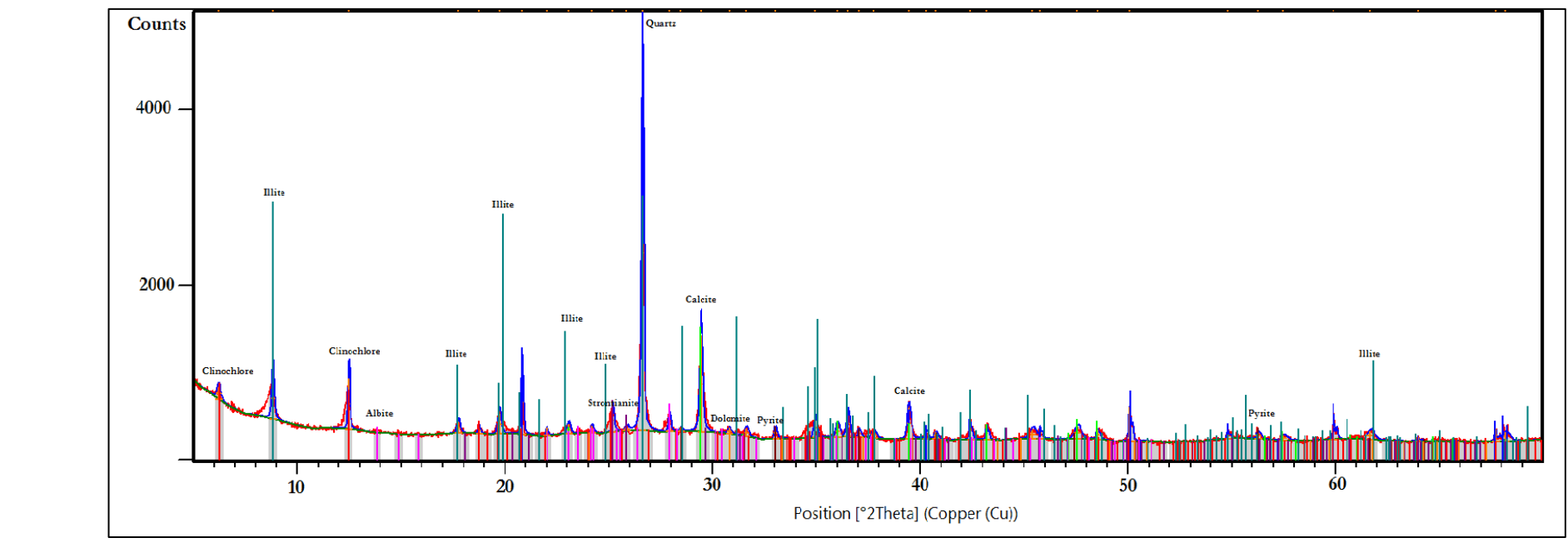
Table(1): Samples and their corresponding depths, formations, leachates and type

Sample Number	Depth (ft)	Formation	Leachate Used	Type
M1	8549 ft	Point Pleasant	Water	Core
M2	8549 ft	Point Pleasant	Acid	Core
M3	8479 ft	Point Pleasant	Water	Core
M4	8479 ft	Point Pleasant	Acid	Core
M5	8470 ft-8500 ft	Utica	Water	Cuttings
M6	8500 ft-8530 ft	Utica	Water	Cuttings
M7	8530 ft-8560 ft	Utica	Water	Cuttings
M8	8470 ft-8500 ft	Utica	Acid	Cuttings
M9	8500 ft-8530 ft	Utica	Acid	Cuttings
M10	8530 ft-8560 ft	Utica	Acid	Cuttings

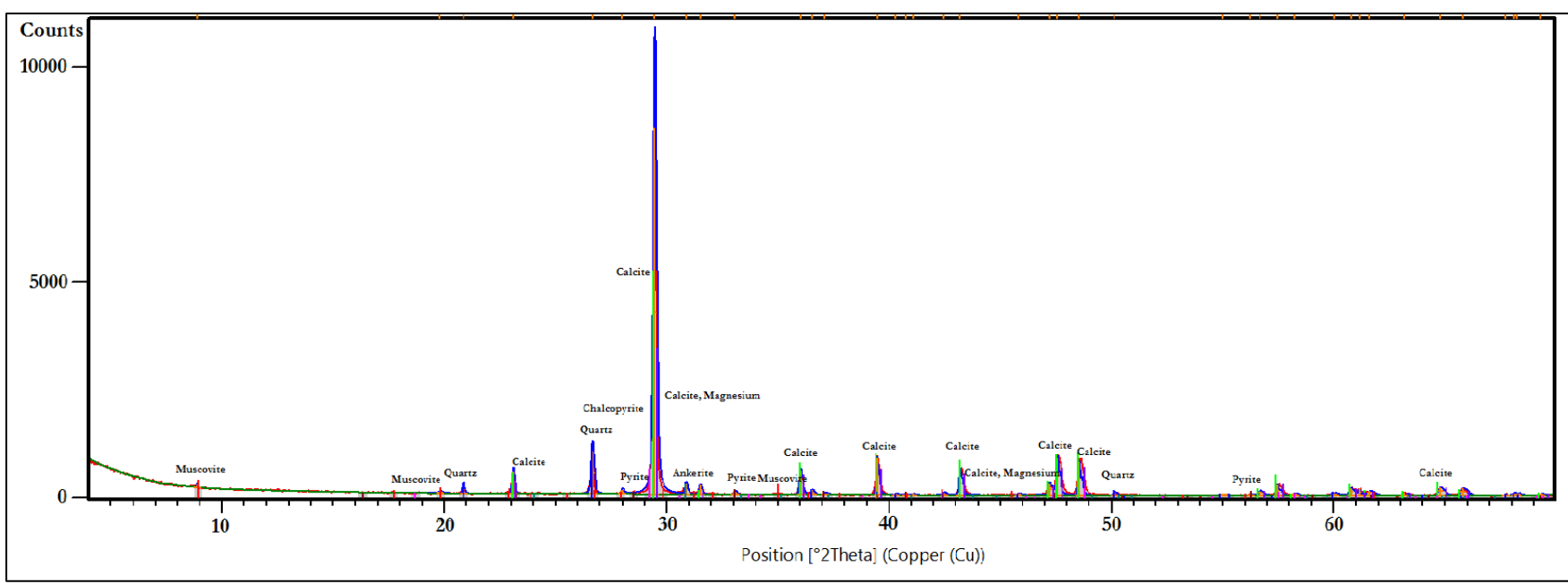
- All samples leached sequentially for 1 day, 2 days, 2 weeks and 3 weeks respectively.
- X-Ray Diffraction (XRD)** for bulk mineralogy pre-leaching.
 - PANalytical X’Pert Pro X-ray diffractometer.
 - Data collection: X’Celerator detector run from 4 to 70 degrees 2-theta with a voltage of 45 keV and tube current of 40 mA (CuKα radiation).
 - Data analysis: PANalytical HighScore Plus peak search.
- Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectrometry (EDXS)** for mineral-textural and elemental data post-leaching.
 - FEI Quanta 250 Field Emission SEM
 - Bruker Xflash Energy Dispersive X-Ray Spectrometer.
 - Sample prep: Au/Pd with a Denton Desk V precious metal sputter coater.
 - Images: Acquired using a BSE detector and secondary electron detector with a voltage of 15keV, working distance ~13mm and spot size 4.0.
- Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)** for major and trace element concentrations (sequential leaching).
- Ion Chromatography** for anion concentrations (sequential leaching).
- PHREEQC geochemical modeling** to determine saturation indices of selected phases (version 3.1.7-9213).

Results

- X-Ray Diffraction:**
 - Utica Formation cuttings samples have clay-rich composition (Fig 1).
 - illite, muscovite, chlorite
 - Point Pleasant Formation core samples have carbonate-rich composition (Fig 2).
 - calcite, dolomite with minor clays and pyrite

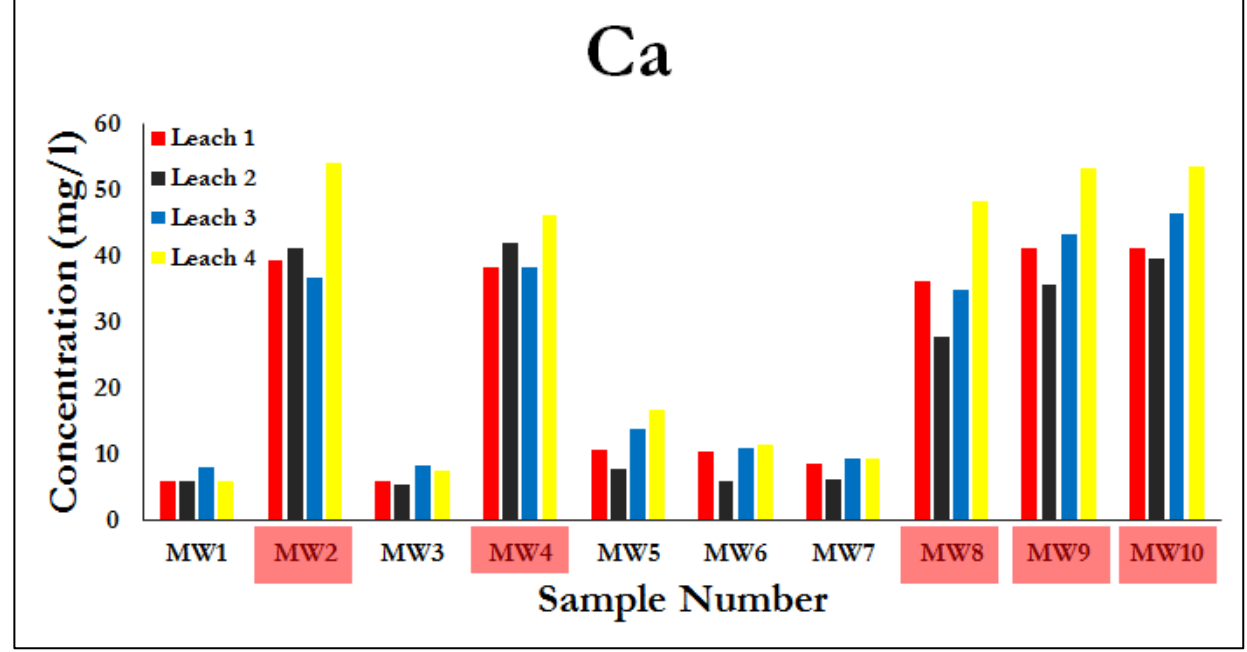


Figure(1): XRD scan for cuttings depth 8680 ft–8710 ft (one-quarter divergence slit)

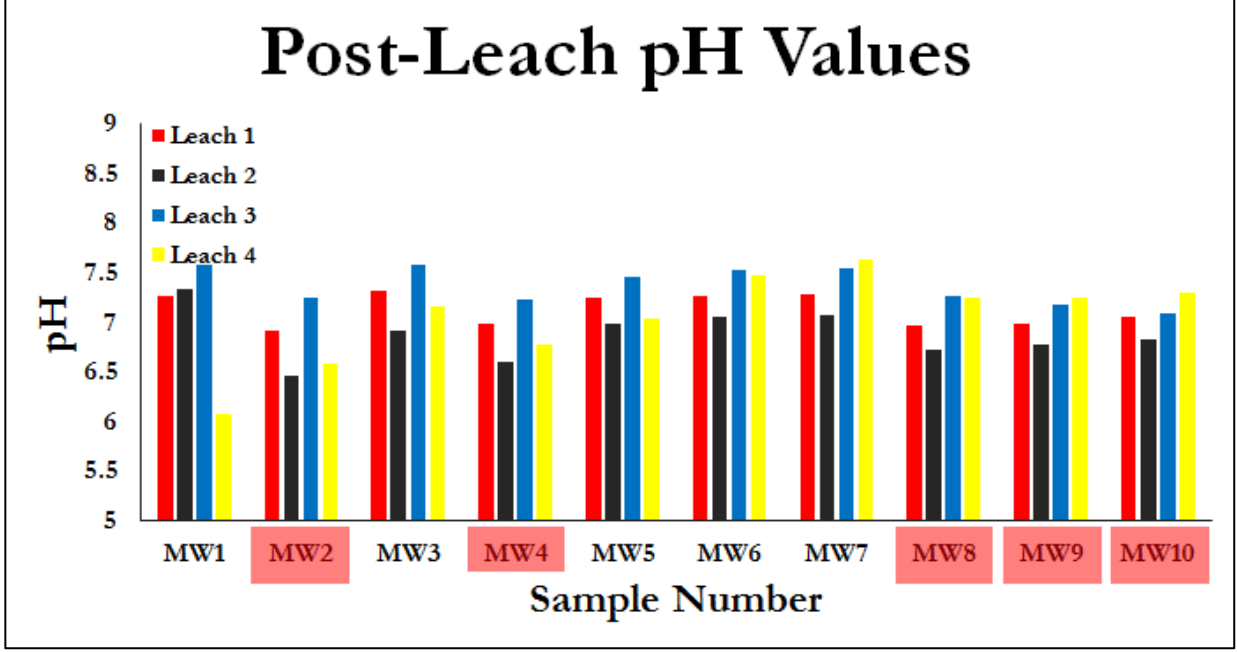


Figure(2): XRD scan for core (predominately fine-grained matrix) depth 8479 ft

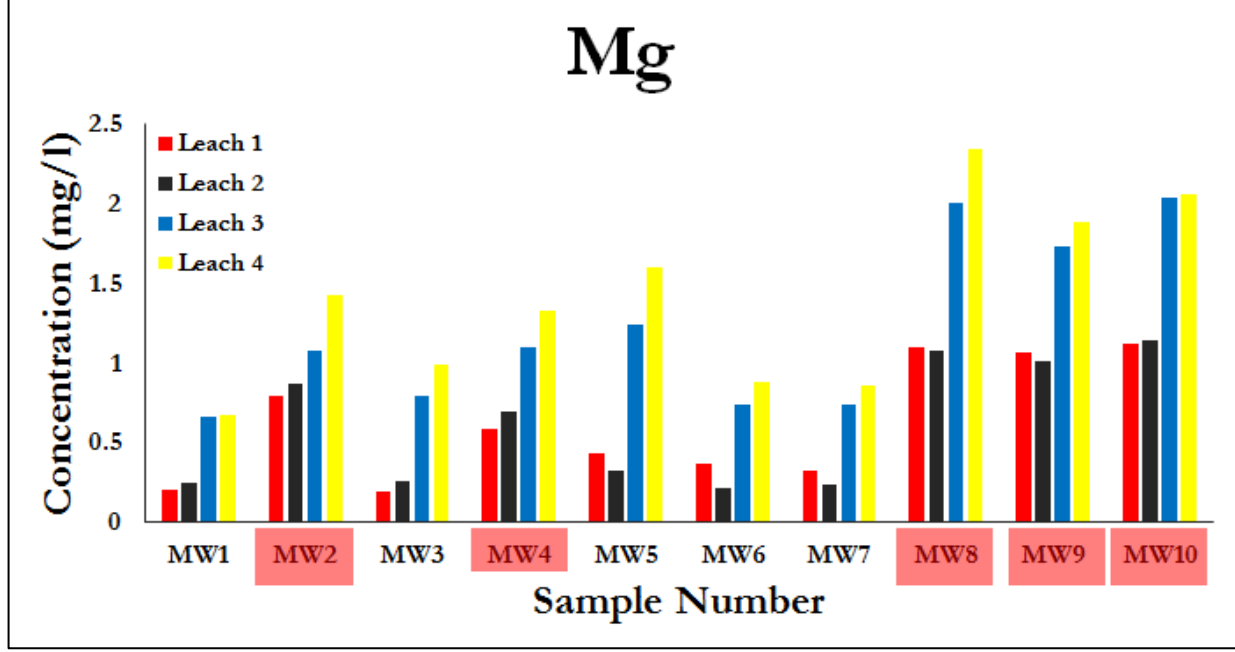
Sequential Leach Experiments:



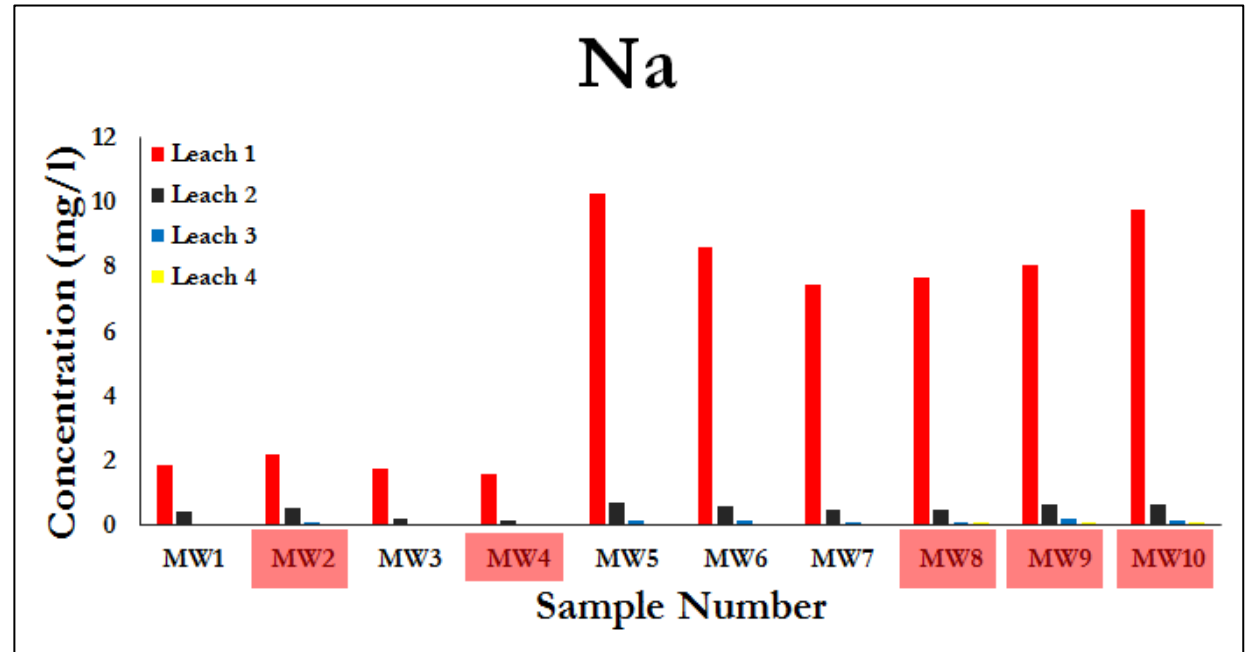
Figure(3): Calcium concentrations M1-M10 Leaches 1-4



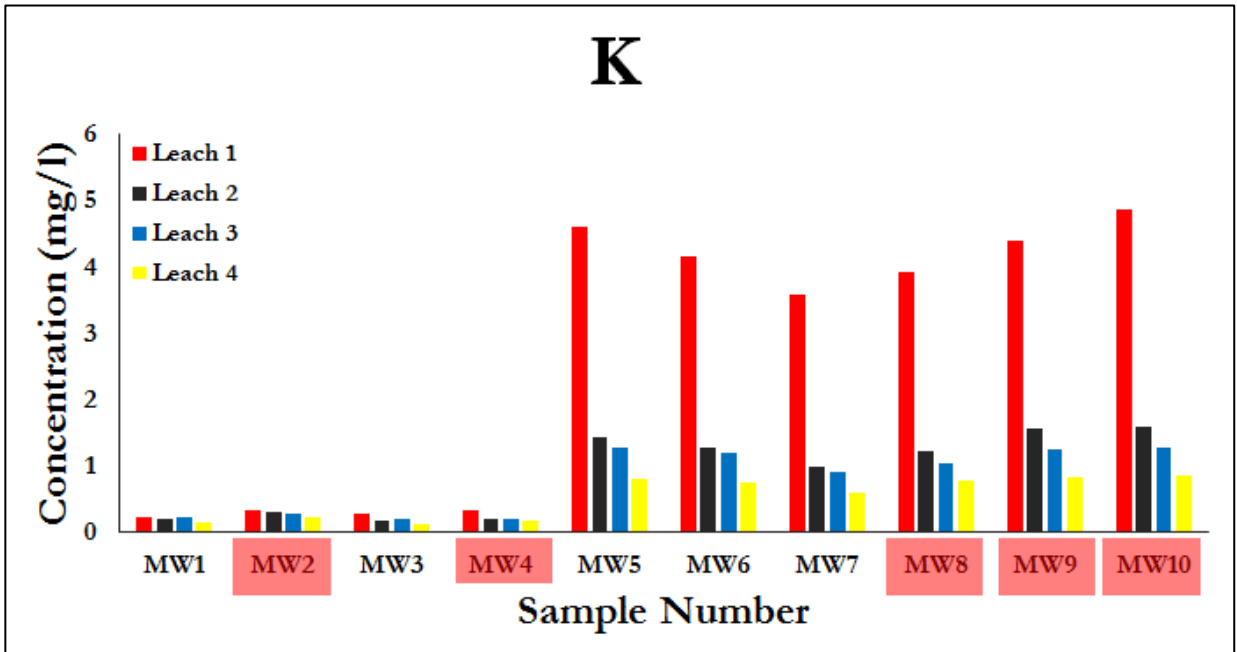
Figure(4): Post-leach pH values



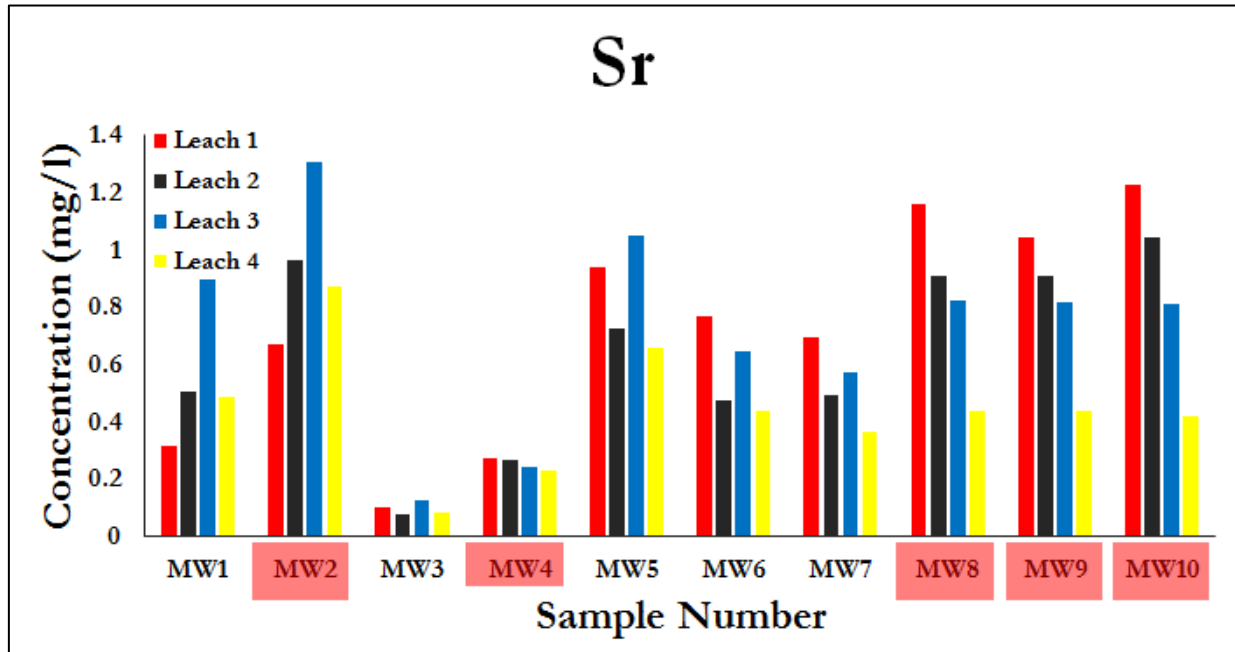
Figure(5): Magnesium concentrations M1-M10 Leaches 1-4



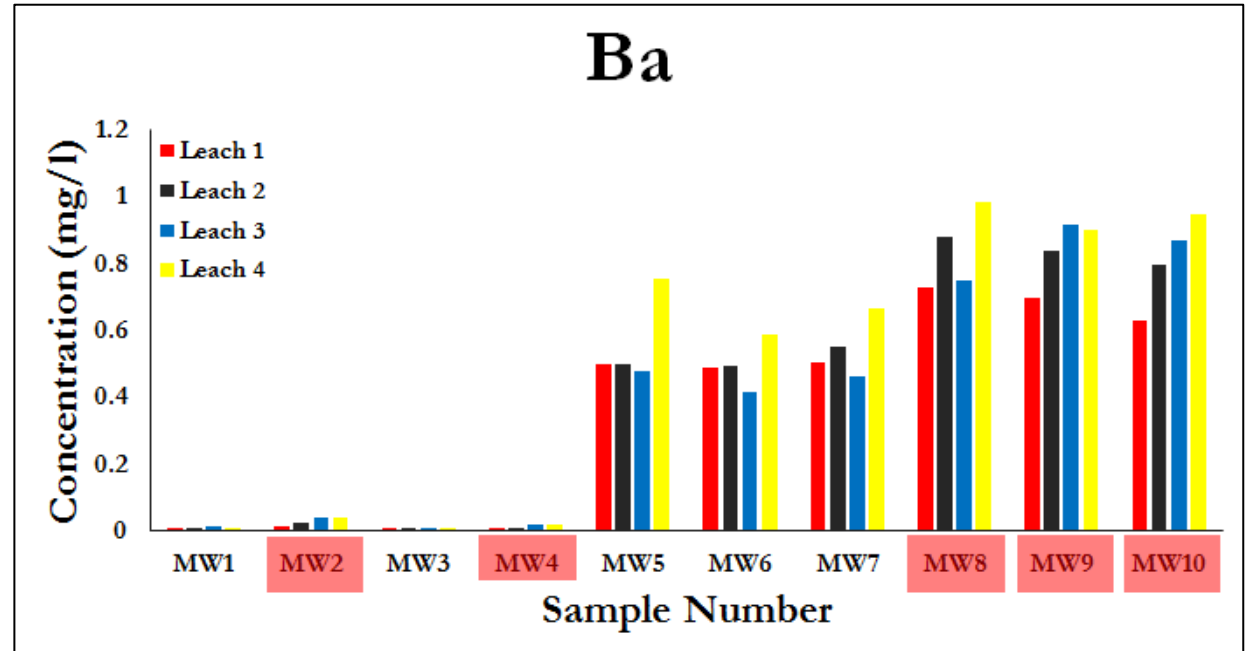
Figure(6): Sodium concentrations M1-M10 Leaches 1-4



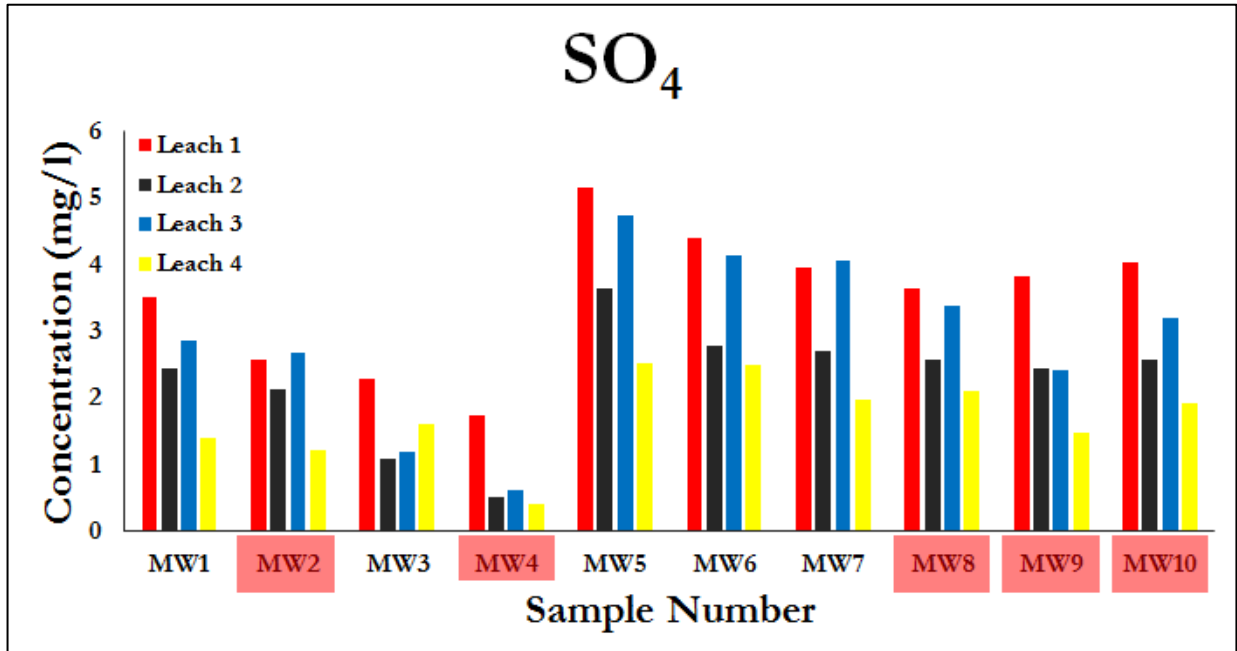
Figure(7): Potassium concentrations M1-M10 Leaches 1-4



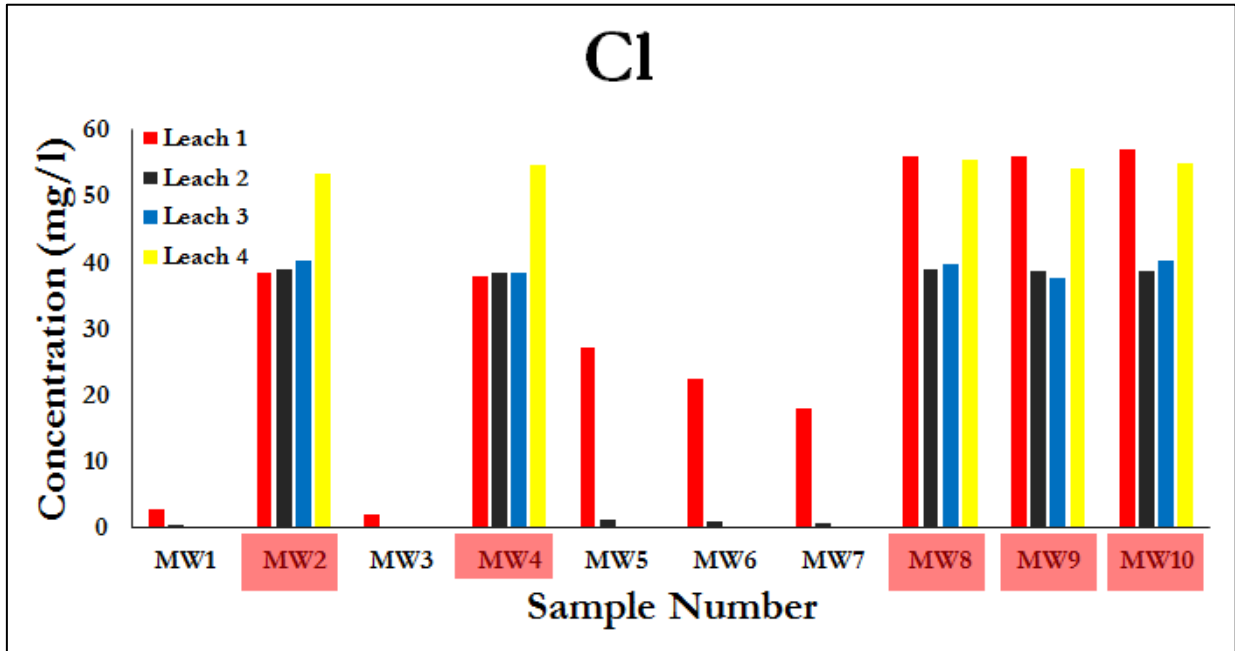
Figure(8): Strontium concentrations M1-M10 Leaches 1-4



Figure(9): Barium concentrations M1-M10 Leaches 1-4



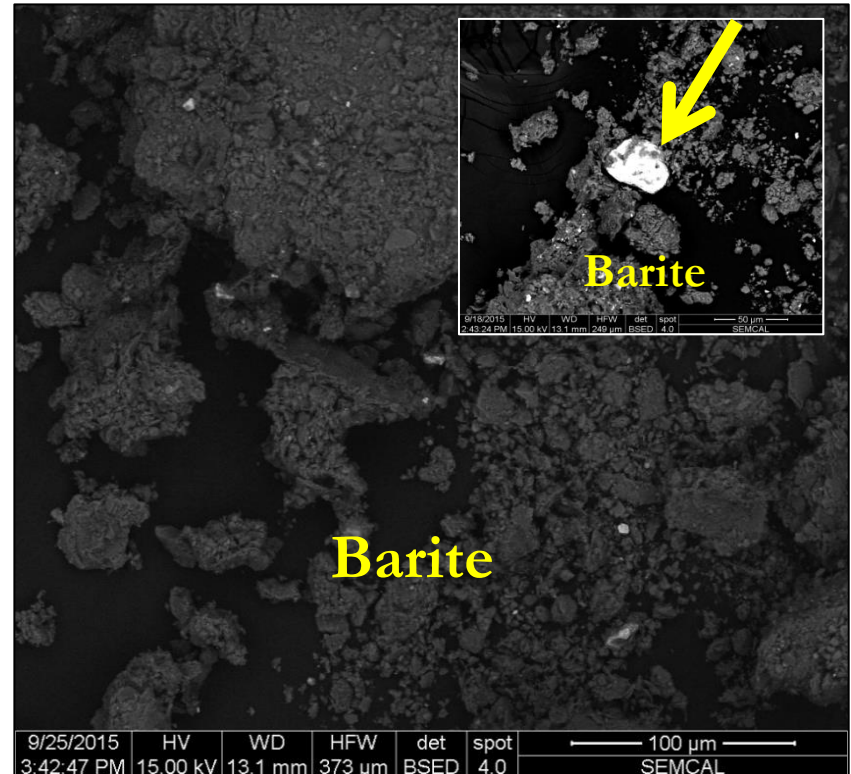
Figure(10): Sulfate concentrations M1-M10 Leaches 1-4



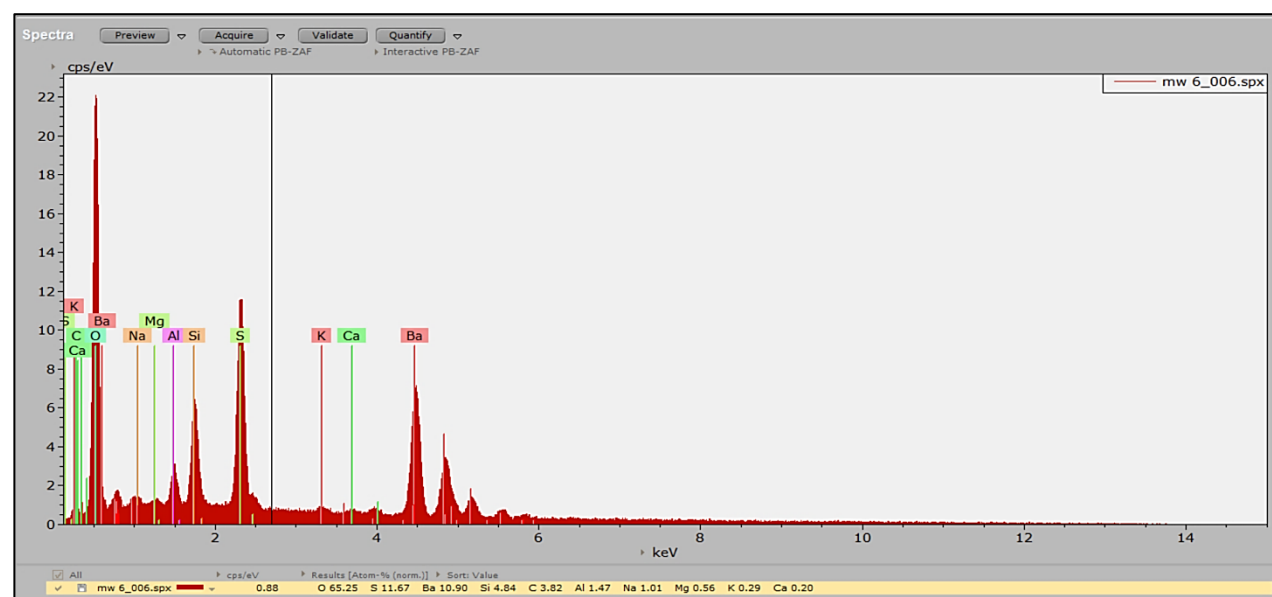
Figure(11): Chloride concentrations M1-M10 Leaches 1-4

- Total solute released from the solid phase was greater in 1mM HCl than in water for both core and cuttings samples.
- Cuttings samples in general had much higher solute concentrations than core using both water and acid leachates.
- Rapid change in pH after ~1 day suggests neutralization by carbonate dissolution.
 - The dissolution of calcite in acid can be written as follows:
$$CaCO_3 + 2H^+ \leftrightarrow Ca^{2+} + CO_2 + H_2O \quad (1)$$
 - The dissolution of dolomite in acid can be written as follows:
$$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O \quad (2)$$

Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometry:



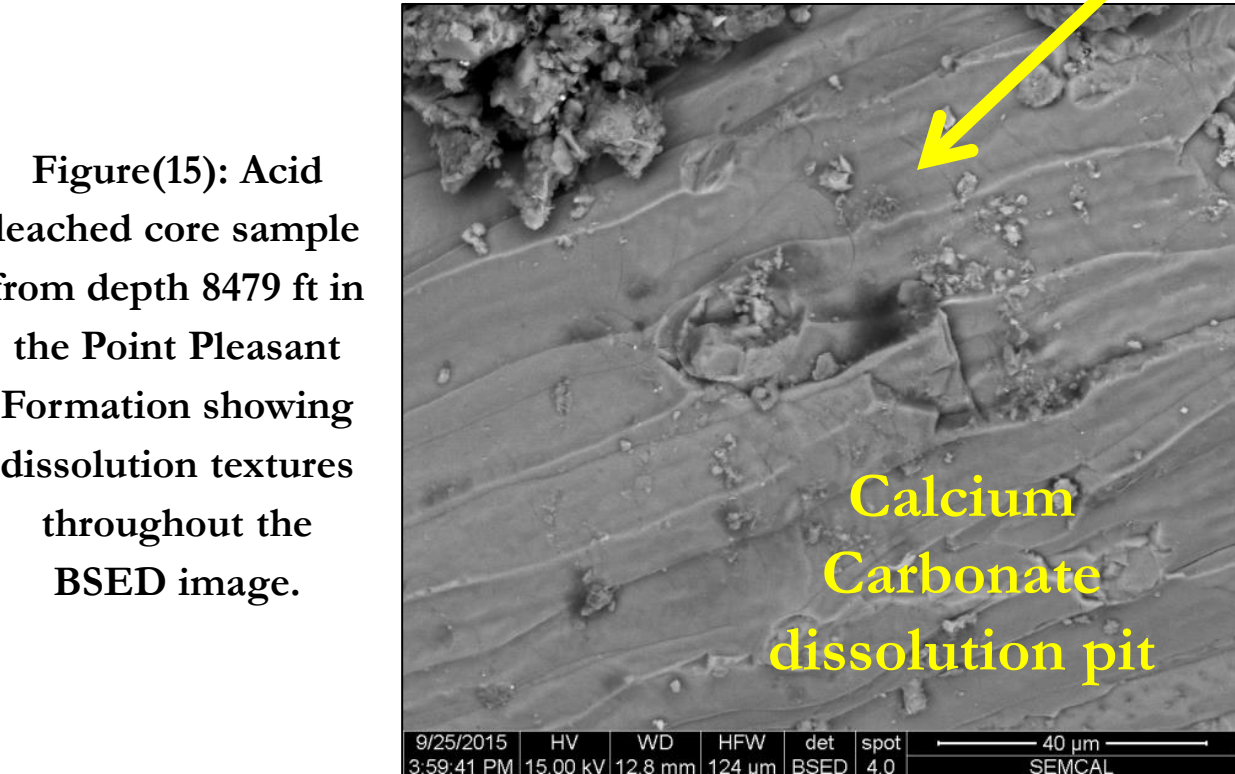
Figure(12): Cuttings water sample from depth 8500 ft-8530 ft in the Utica Formation showing a large, euhedral barite grain with smaller grains throughout the BSED image.



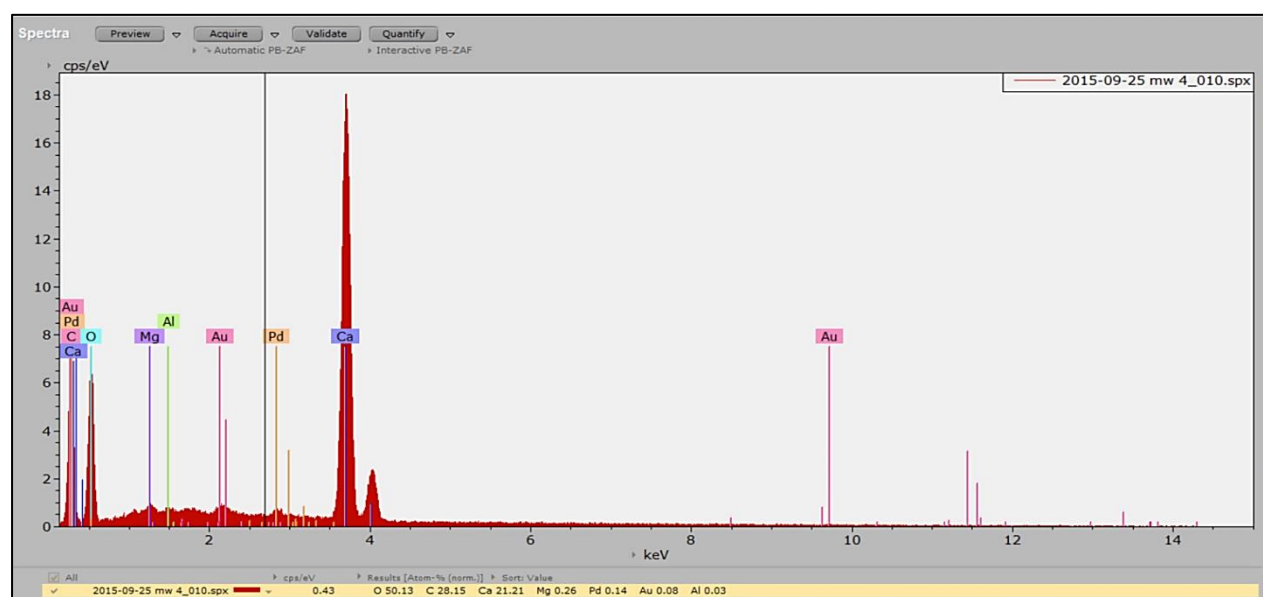
Figure(14): EDXS data identifying barite in post-leach cuttings sample from depth 8500 ft-8530 ft in the Utica Formation. Spot analysis was taken on the large, euhedral grain presented in Figure 12.



Figure(17): FEI Quanta 250 SEM (fci.com)



Figure(15): Acid leached core sample from depth 8479 ft in the Point Pleasant Formation showing dissolution textures throughout the BSED image.



Figure(16): EDXS data showing calcium carbonate of acid leached core sample from depth 8479 ft in the Point Pleasant Formation.

- SEM analysis showed that cutting samples showed large amounts of barite still present in the samples after leaching with water and acid.
- SEM analysis showed evidence of dissolution pits in calcite in core acid samples.

Conclusions

- Core and cuttings samples both release salts in the leaching experiments. Salt content was greater in the cuttings than core samples due to contamination from drilling fluids.
- The major source of Ca and Mg in fluid samples is from the dissolution of calcite and dolomite in the formations.
- The *additional* source of magnesium in leach experiments with the cuttings samples could be from chlorite dissolution which was identified by XRD.
- Barite was introduced during the drilling process which results in a striking difference in Ba concentration between core and cuttings samples
- Most leach experiments were saturated with respect to barite suggesting barite solubility is limiting Ba release to solution.
- The initial release of K in the cuttings leach experiments may have originated from a mix of formation brine and drilling muds. The lower subsequent K release from core and cuttings most likely originates from the dissolution of illite/muscovite clay phases present in the formations.
- The source of strontium is predominately from the dissolution of carbonates because its behavior is similar to calcium and magnesium.

Future Work

Presently, sequential leach experiments are being performed on a new set of samples. All samples being used are from the same core and cutting depths as the core and cutting samples used for this thesis experiment. The experiment in progress follows the procedures of a similar experiment performed by Stewart et al. (2015)² in which fluids injected during hydraulic fracturing are replicated in a lab. This allows the results of this thesis experiment to be taken a step further.

- Water leach
 - Extract soluble salts and evaporated pore water.
- Ammonium acetate leach
 - Extract surface exchangeable and low-charge interlayers.
- 8% Acetic acid leach
 - Extract carbonate minerals.
- 0.1 M HCl
 - Extract high-charge interlayers and partial silicate/oxides.

References

¹Blauch, M. E., Houston, N. A., Lipinski, B. A., Moore, T. R., & Meyers, R. R. (2009). Marcellus Shale Post-Frac Flowback Waters – Where is All the Salt Coming From and What are the Implications? *Society of Petroleum Engineers*

²Stewart, B. W., Chapman, E. C., Capo, R. C., Johnson, J. D., Graney, J. R., Kirby, C. S., et al. (2015). Origin of brines, salts and carbonate from shales of the Marcellus Formation: Evidence from geochemical and Sr isotope study of sequentially extracted fluids. *Applied Geochemistry*, 60, 78-88.

Acknowledgements

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